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Mass balance and isotope effects during nitrogen transport through septic tank systems with packed-bed (sand) filters

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ABSTRACT

Septic tank systems are an important source of NO_3^- to many aquifers, yet characterization of N mass balance and isotope systematics following septic tank effluent discharge into unsaturated sediments has received limited attention. In this study, samples of septic tank effluent before and after transport through single-pass packed-bed filters (sand filters) were evaluated to elucidate mass balance and isotope effects associated with septic tank effluent discharge to unsaturated sediments. Chemical and isotopic data from five newly installed pairs and ten established pairs of septic tanks and packed-bed filters serving single homes in Oregon indicate that aqueous solute concentrations are affected by variations in recharge (precipitation, evapotranspiration), NH_4^+ sorption (primarily in immature systems), nitrification, and gaseous N loss via NH_3 volatilization and (or) N_2 or N_2O release during nitrification/denitrification. Substantial NH_4^+ sorption capacity was also observed in laboratory columns with synthetic effluent. Septic tank effluent $\delta^{15}\text{N}\text{-NH}_4^+$ values were almost constant and averaged $+4.9\text{‰} \pm 0.4\text{‰}$ (1σ). In contrast, $\delta^{15}\text{N}$ values of NO_3^- leaving mature packed-bed filters were variable ($+0.8$ to $+14.4\text{‰}$) and averaged $+7.2\text{‰} \pm 2.6\text{‰}$. Net N loss in the two networks of packed-bed filters was indicated by average 10–30% decreases in Cl^- -normalized N concentrations and 2–3% increases in $\delta^{15}\text{N}$, consistent with fractionation accompanying gaseous N losses and corroborating established links between septic tank effluent and NO_3^- in a local, shallow aquifer. Values of $\delta^{18}\text{O}\text{-NO}_3^-$ leaving mature packed-bed filters ranged from -10.2 to -2.3‰ (mean $-6.4\text{‰} \pm 1.8\text{‰}$), and were intermediate between a $2/3\text{ H}_2\text{O}\text{-O} + 1/3\text{ O}_2\text{-O}$ conceptualization and a 100% $\text{H}_2\text{O}\text{-O}$ conceptualization of $\delta^{18}\text{O}\text{-NO}_3^-$ generation during nitrification.

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1. Introduction

Approximately 23% of U.S. homes use septic tanks for wastewater disposal (U.S. Census Bureau, 2005), often leading to degradation of ground water quality (Reneau et al., 1989). Packed-bed filters are commonly used to facilitate the dispersal of septic tank effluent, particularly in areas with shallow water tables. Packed-bed filters consist of sediment mounds built on top of the native ground surface. Septic tank

effluent processing occurs primarily in a $\geq 60\text{-cm}$ -thick sand layer. Basal gravel for drainage and a soil cap on top bring the total height to about 1 m. In properly operating packed-bed filters, reduced forms of N are oxidized to NO_3^- (Crites and Tchobanoglous, 1998). Packed-bed filters are considered “essentially aerobic” (USEPA, 2002) at macroscopic scales. Thus, packed-bed filters serve as artificial unsaturated zones, and as such, provide opportunities for characterizing chemical and isotopic effects during solute transport from septic tanks

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to unsaturated sediments in the absence of complications from other large chemical sources such as fertilizers.

Apparent N loss in single-pass (non-recirculating) packed-bed filters serving single homes and other small decentralized facilities has been observed in numerous studies (Brandes, 1980; Ronayne et al., 1984; Bushman, 1996; Crites and Tchobanoglous, 1998; Harrison et al., 2000; Bayley et al., 2003). This apparent N loss has often been attributed to denitrification or NH_4^+ sorption (used in this paper to describe both specific adsorption and ion exchange). However, evidence to support denitrification or sorption has been scant. Also, timescales over which N attenuation mechanisms may operate have not always been well characterized; this has implications for interpretation of packed-bed filter data insofar as early-time NH_4^+ sorption prior to sorption site saturation may bias results if studies occur over timescales shorter than those required to achieve sorption site saturation. Furthermore, effects of dilution with precipitation (rain, snowmelt) or concentration in response to evapotranspiration are often ignored. Thus, some of the apparent N loss observed in studies of packed-bed filters may in fact reflect dilution rather than an actual loss due to a removal process such as volatilization, denitrification, or sorption. The distinction between sorption and volatilization or denitrification is important because volatilization and denitrification essentially remove N from the packed-bed filter, whereas sorbed NH_4^+ remains in the reactive fixed N pool at the site and may be remobilized.

The purpose of this study was to characterize N losses and the associated isotopic effects that occur in single-pass packed-bed filters used for single-family septic tank effluent disposal. The focus was on field investigations, in which a combination of newly installed and mature packed-bed filters provided data on temporal aspects of packed-bed filter performance. Cl^- concentrations were used to normalize N concentrations to account for effects of dilution and evapotranspiration. Stable isotope analyses of N and O in NH_4^+ , NO_2^- , and H_2O provide additional evidence for solute fate and document the nature and variability of isotopic signatures of septic tank-derived NO_3^- that may enter ground water. Laboratory sand column sorption experiments complemented the field investigations.

2. Study design and methods

In this study, five newly installed packed-bed filters in the vicinity of La Pine, Oregon, were monitored over a period of years to provide information on maturing (through mature phase) packed-bed filters. Ten additional packed-bed filters in the vicinity of Bend, Oregon, were sampled once to provide additional information on mature systems (0.9 to 9.1 yr of operation). Coarse volcanic sand from a packed-bed filter under construction near La Pine was used in laboratory column experiments.

2.1. Study area

La Pine and Bend are located in Oregon's upper Deschutes Basin (Fig. 1). Septic tanks are used in both areas, with particularly widespread use in the rural-residential commu-



Fig. 1 – Map of Oregon showing the locations of the packed-bed filter networks near La Pine (maturing network) and Bend (mature network).

nity of La Pine. As of 2004, 6550 homes in the La Pine area were served by septic tanks, at least 900 of which were connected to packed-bed filters (B.J. Rich, Deschutes County Environmental Health Division, written commun., 2008). Local geology consists of Quaternary and Tertiary basaltic and andesitic flows, vent deposits, and pyroclastic rocks, and (chiefly volcanic) sediment. Precipitation, ranging from about 40 to 50 cm/yr over most of the La Pine area and 20 to 40 cm/yr near Bend (Taylor, 1993), falls primarily from November through March. Mean annual air temperatures are similar: 7.2 °C near La Pine and 8.0 °C near Bend.

2.2. Maturing packed-bed filters

Deschutes County Environmental Health Division (DCEHD) and Oregon Department of Environmental Quality (ODEQ) installed five single-pass packed-bed filters in the La Pine area during fall 2000. Three of the new systems (53110A, 17346B, 17186H) contained polyvinyl chloride half-pipes at the bottom that emptied into collection buckets (representing “bottomless” systems commonly used in the region of the study); the other two (50663F, 52330S) were installed with plastic liners on the bottom that fed into collection chambers (representing “lined” systems commonly used in the region). Samples of septic tank fluid (considered equivalent to septic tank effluent and referred to as such in this paper) and packed-bed filter effluent were collected, usually as paired samples, approximately six times per year between late 2000 and late 2003. Samples were analyzed for N species and Cl^- . The resulting data set (Oregon Department of Environmental Quality, 2005) provides temporal characterization of packed-bed filter effluent from early in their operation into a period of apparent maturity, and thus these packed-bed filters are referred to as the maturing packed-bed filter network. For this study, we used samples with complete analyses of $\text{NO}_2^- + \text{NO}_3^-$, NH_4^+ , Kjeldahl N (NH_4^+ plus organic N), and Cl^- . Because NO_2^- typically represents a negligible component of $\text{NO}_2^- + \text{NO}_3^-$, we henceforth refer to $\text{NO}_2^- + \text{NO}_3^-$ as NO_3^- . NO_2^- concentrations in four packed-bed filter samples, collected May 31, 2001, and analyzed by the U.S. Geological Survey (USGS), were 0.03% to 0.34% of $\text{NO}_2^- + \text{NO}_3^-$.

Additional samples were collected for analysis of N and O isotopes in NH_4^+ , NO_3^- , and H_2O . Samples of septic tank effluent

were analyzed for $\delta^{15}\text{N-NH}_4^+$ and packed-bed filter effluent for $\delta^{15}\text{N-NO}_3^-$.

Samples were collected by dipping clean bottles into the centroid of the septic tank chamber or packed-bed filter collection bucket, and sub-sampling from this primary collection bottle. Samples for N speciation were unfiltered and preserved with H_2SO_4 to $\text{pH} < 2$ (plus refrigeration). Samples for isotope analysis were filtered ($0.45 \mu\text{m}$) and either preserved with H_2SO_4 to $\text{pH} < 2$ (plus refrigeration) (NH_4^+) or with KOH to $\text{pH} > 11$ (plus freezing) (NO_3^-). Samples for Cl^- analysis were filtered.

N and Cl^- concentrations were analyzed by ODEQ in Portland, Oregon: NO_3^- by automated cadmium reduction; NH_4^+ by automated phenate; Kjeldahl N by Kjeldahl digestion and colorimetry (automated phenate); Cl^- by automated ferricyanide (Clesceri et al., 1998). Method reporting levels for N species were: NO_3^- , 0.01 mg N/L; NH_4^+ , 0.02 mg N/L; and Kjeldahl N, 0.2 mg N/L. Total N was calculated as NO_3^- plus Kjeldahl N.

N isotopes in NH_4^+ , N and O isotopes in NO_3^- , and H and O isotopes in H_2O were analyzed by isotope-ratio mass spectrometry at the USGS Reston Stable Isotope Laboratory (<http://isotopes.usgs.gov>) by modifications of methods described previously (Supplementary data). $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values are reported relative to N_2 in air and O in VSMOW, respectively, and normalized to published values for international isotopic reference materials (Supplementary data).

In addition to routine ambient monitoring by DCEHD/ODEQ, DCEHD collected an additional set of samples from four of these sites on May 31, 2001. These samples were filtered (DCEHD) and analyzed (USGS) for N and Cl^- concentrations, and N isotopes. Samples for N species were preserved by chilling (4°C). Kjeldahl N was analyzed by automated-segmented flow colorimetry (Fishman, 1993). Analytical methods for NO_3^- , NH_4^+ , and Cl^- concentrations were identical to those used in the column experiments (below). Samples for isotope analysis were preserved and analyzed as described above.

2.3. Mature packed-bed filter synoptic

DCEHD and ODEQ sampled 10 existing, single-pass, packed-bed filter systems in October, 2001. These packed-bed filters were identical in structure to the lined packed-bed filters in the maturing packed-bed filter network; they were chosen because their ages (duration of use: 0.9 to 9.1 years) were likely to have resulted in mature conditions, and all systems had sampling access. Techniques of sample collection, processing, and analysis were identical to those used for the maturing packed-bed filter network. This part of the study is referred to as the mature packed-bed filter network.

2.4. Column experiments

Sorption of NH_4^+ to packed-bed filter sediment was evaluated with a 76-cm tall, 9.5-cm inside diameter acrylic column under unsaturated conditions using synthetic septic tank effluent containing NH_4HCO_3 and NaCl . The sorption experiment was followed by a desorption experiment with 2 M KCl . An additional experiment was done to measure pre-existing

exchangeable NH_4^+ on fresh packed-bed filter sediment. Experimental details and analytical methods are described in the Supplementary data.

3. Results and discussion

3.1. NH_4^+ sorption in sand columns

No detectable NH_4^+ was present in water exiting the sediment column during the sorption experiment with synthetic septic tank effluent (Fig. 2a). Based on Cl^- breakthrough, over 10 (partially saturated) pore volumes passed through the column during the sorption experiment, which ran for approximately 6 days. No NO_3^- was detected in the column effluent, suggesting that nitrification was negligible, and thus indicating that sorption was likely responsible for the observed NH_4^+ attenuation. The absence of measurable nitrification may reflect the lack of introduction of nitrifying bacteria from septic tank effluent and the short timeframe for any endogenous sediment-bound nitrifying bacteria to multiply.

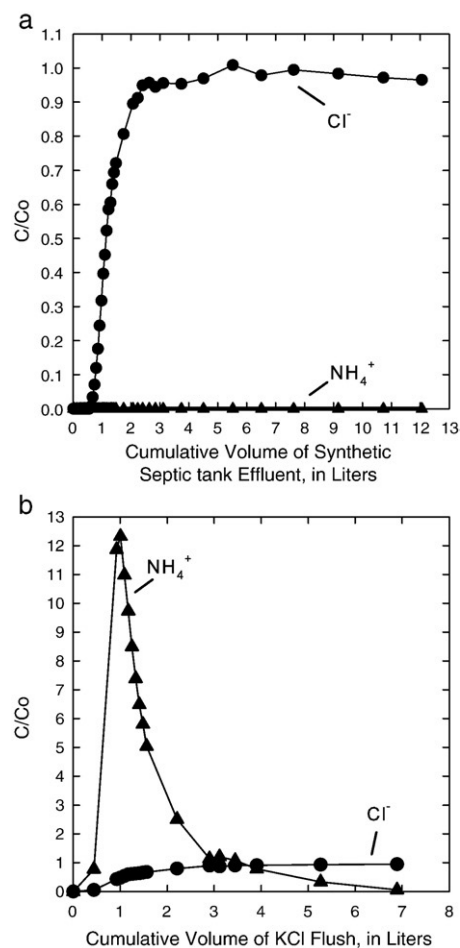


Fig. 2 – Breakthrough curves for sand column experiments with synthetic septic tank effluent. (a) Sand column NH_4^+ adsorption. (b) Sand column NH_4^+ desorption using 2 M KCl . C = concentration exiting column; C₀ = concentration entering column.

Column effluent near the end of the sorption experiment, at 10.72 L cumulative volume of effluent, contained cations not added to the synthetic septic tank effluent: Ca^{2+} (30.8 mg/L), Mg^{2+} (19.8 mg/L), and K^+ (9.13 mg/L). These cations probably represent cations exchanged during NH_4^+ sorption, although mineral and volcanic glass dissolution also may have contributed to some extent.

NH_4^+ strongly sorbs to mineral surfaces (Hem, 1985), and clay minerals play a particularly important role in NH_4^+ sorption reactions (Nommik and Vahtras, 1982). However, large amounts of clay are not required for measurable NH_4^+ sorption, and considerable NH_4^+ retardation has been observed in coarse-grained aquifers with low (<0.1%) clay content (Ceazan et al., 1989; Buss et al., 2004; Böhlke et al., 2006). Thus, the essentially complete apparent sorption of NH_4^+ during the course of this experiment, although done with coarse sand containing only 0.4% silt and clay (Table S1 in Supplementary data), is not unexpected.

The desorption experiment was done to determine if NH_4^+ that was presumed to have sorbed to sediment surfaces could be desorbed. KCl treatment released a large pulse of NH_4^+ , confirming the hypothesis that the attenuated NH_4^+ had been sorbed (Fig. 2b). By the termination of the desorption experiment, 97% of the sorbed NH_4^+ had been recovered, indicating that sorption was essentially fully reversible.

To evaluate the possibility that some of the desorbed NH_4^+ might have been NH_4^+ that was attached to sediment surfaces prior to the sorption experiment, a column was packed with fresh sediment and subjected to 2 M KCl treatment. No NH_4^+ was detected in the effluent, indicating that prior to introduc-

tion of synthetic septic tank effluent, the column contained <1% of the exchangeable NH_4^+ -N loaded and subsequently desorbed from the column during the synthetic effluent experiments.

Laboratory column experiments with synthetic septic tank effluent provided information on early-time (transient) behavior of NH_4^+ in sand. However, this process eventually may be limited by sorption capacity, and nitrification is an important process in properly functioning mature septic systems. Therefore, longer-term monitoring with real septic tank effluent is needed to provide more comprehensive understanding of N behavior in packed-bed filters.

3.2. N and Cl^- fluxes from packed-bed filters

Septic tank effluent consisted almost entirely of reduced N (Table 1 and Supplementary data). N from septic tank effluent was oxidized efficiently within packed-bed filters, and NO_3^- was the primary N species in recharge to ground water from packed-bed filters, particularly for mature systems. For example, for samples collected after the first year of operation in the maturing packed-bed filter network, >99% (median and mean) of total N in septic tank effluent was reduced N ($n=63$), whereas 98% (median and mean) of total N in packed-bed filter effluent was NO_3^- ($n=63$). Most N and Cl^- in these samples was introduced during household water use. Ground water used for domestic purposes in the vicinity of the maturing network currently is dilute, typically containing <1 mg N/L of NO_3^- and <4 mg/L of Cl^- (Hinkle et al., 2007), whereas concentrations in packed-bed filter effluent are considerably greater: NO_3^- , 55 mg

Table 1 – Chemical and isotopic data from the mature packed-bed filter network

Site	Sample	Date	System age (years)	NO_3^- (mg N/L)	NH_4^+ (mg N/L)	TKN ^a (mg N/L)	Cl^- (mg/L)	$\delta^{15}\text{N-NH}_4^+$	$\delta^{15}\text{N-NO}_3^-$	$\delta^{18}\text{O-NO}_3^-$	$\delta^{18}\text{O-H}_2\text{O}$	$\delta^2\text{H-H}_2\text{O}$
								(‰)	(‰)	(‰)	(‰)	(‰)
26154	Septic tank	10/10/2001		0.017	35	45	40	5.6				
26154	Packed-bed filter	10/10/2001	0.9	35.7	0.50	0.6	50		7.3	-6.4	-13.27	-103.2
26165	Septic tank	10/23/2001		0.035	42	57	61	5.5				
26165	Packed-bed filter	10/23/2001	1.5	51.7	0.04	0.7	71		10.5	-6.4	-13.61	-104.2
26149	Septic tank	10/23/2001		0.013	21	30	14	4.8				
26149	Packed-bed filter	10/23/2001	9.1	23.9	0.06	5.4	16		5.1	-7.1		
26162	Septic tank	10/23/2001		0.035	53	64	35	4.9				
26162	Packed-bed filter	10/23/2001	1.9	41.4	0.88	2.8	38		8.0	-7.1		
26180	Septic tank	10/24/2001		0.028	33	70	30	4.7				
26180	Packed-bed filter	10/24/2001	2.8	47.8	0.83	3.3	30		14.4	-4.6	-14.50	-109.0
26171	Septic tank	10/24/2001		0.025	43	54	27	5.2				
26171	Packed-bed filter	10/24/2001	2.2	26.5	0.21	1.6	27		10.4	-6.3	-12.84	-97.9
26182	Septic tank	10/26/2001		0.023	26	34	17	5.2				
26182	Packed-bed filter	10/26/2001	5.8	22.6	0.05	0.6	19		7.9	-7.5	-14.46	-107.6
26159	Septic tank	10/26/2001		0.016	29	69	55	5.4				
26159	Packed-bed filter	10/26/2001	1.8	47.8	0.08	1.1	63		7.8	-3.2	-13.96	-103.9
26144	Septic tank	10/26/2001		0.026	29	62	28	4.6				
26144	Packed-bed filter	10/26/2001	2.3	46.6	0.04	1.1	26		7.5	-5.1	-14.38	-104.4
26178	Septic tank	10/26/2001		0.013	28	44	14	4.5				
26178	Packed-bed filter	10/26/2001	2.6	36.7	<0.02	5.1	16		6.4	-4.2	-13.77	-95.4

$\delta^{15}\text{N-NH}_4^+$ data normalized to +0.4‰ for IAEA-N1 and +53.7‰ for USGS26; $\delta^{15}\text{N-NO}_3^-$ data normalized to +4.7‰ for IAEA-N3 and +180.0‰ for USGS32; $\delta^{18}\text{O-NO}_3^-$ data normalized to -27.9‰ for USGS34 and +25.6‰ for IAEA-N3; $\delta^{18}\text{O-H}_2\text{O}$ data normalized to 0.00‰ for VSMOW and -55.50‰ for SLAP; $\delta^2\text{H-H}_2\text{O}$ data normalized to 0.0‰ for VSMOW and -428.0‰ for SLAP.

^a TKN, total Kjeldahl N.

N/L (median) or 58 mg N/L (mean), and Cl^- , 45 mg/L (median) or 48 mg/L (mean), for the 63 post-first-year maturing-network samples.

In the vicinity of La Pine (maturing network), the estimated average volume of septic tank effluent loaded to packed-bed filters is about 430 L/day (Morgan et al., 2007, p. 22). For the mature network, estimated average septic tank effluent fluxes would be about 25% greater, based upon site-specific occupancy data. At the scale of individual 33 m² packed-bed filters, potential recharge from septic tank effluent (flux prior to evapotranspiration losses) averages about 480 to 600 cm/yr for these systems, greatly exceeding the <50 cm/yr of precipitation that falls on these systems.

3.3. Mass balance and isotope effects in the mature packed-bed filter network

Cl^- data are consistent with an evapotranspiration effect in the mature packed-bed filters (Table 1). The ratio of Cl^- in packed-bed filter effluent to Cl^- in septic tank effluent, for the 10 matched pairs of samples, was 1.13 (median) and 1.10 (mean). We interpret this increase in Cl^- to represent the combined effect of dilution (with precipitation) and concentration (by evapotranspiration) in the packed-bed filters. An alternative explanation—that Cl^- might be mobilized from packed-bed filter sediment surfaces—does not appear likely for <1 m of volcanic sands that have been in use in packed-bed filters for long periods of time. Furthermore, background concentrations of Cl^- on the order of a few mg/L in ground water near and upgradient from these systems (Caldwell, 1998) and the absence of detectable Cl^- in column experiment effluent prior to loading with Cl^- (Fig. 2a) argue against a solid-phase Cl^- source.

Cl^- data were used to calculate N mass balances. Packed-bed filter N attenuation is apparent in Cl^- -normalized N concentrations. The ratio of Cl^- -normalized N in packed-bed filter effluent, $(\text{N}/\text{Cl}^-)_{\text{PBFE}}$, to Cl^- -normalized N in septic tank effluent, $(\text{N}/\text{Cl}^-)_{\text{STE}}$, is a measure of the fraction of original septic tank N remaining in the packed-bed filter effluent after adjusting for evapotranspiration and dilution (N^*):

$$\text{N}^* = \frac{(\text{N}/\text{Cl}^-)_{\text{PBFE}}}{(\text{N}/\text{Cl}^-)_{\text{STE}}} \quad (1)$$

Values of N^* for matched pairs of packed-bed filter effluent and septic tank effluent samples from the mature packed-bed filter network ranged from 0.52 to 0.85, with median 0.69 and mean 0.71.

For this network, septic tank effluent $\delta^{15}\text{N}-\text{NH}_4^+$ ranged from +4.5 to +5.6‰ (median and mean +5.0‰). Packed-bed filter effluent $\delta^{15}\text{N}-\text{NO}_3^-$ ranged from +5.1 to +14.4‰ (median +7.8‰, mean +8.5‰). The differences between the median and mean values of $\delta^{15}\text{N}-\text{NH}_4^+$ for septic tank effluent (+5.0‰) and $\delta^{15}\text{N}-\text{NO}_3^-$ for packed-bed filter effluent (+7.8‰ or +8.5‰) are interpreted to indicate isotopic fractionation, and combined with the approximately 30% decrease in Cl^- -normalized N, are consistent with N loss by a combination of NH_3 volatilization prior to nitrification (Kreitler, 1975, 1979; Hübner, 1986) and N_2 or N_2O release during subsequent nitrification and denitrification within the packed-bed filters

(Delwiche and Steyn, 1970; Hübner, 1986; Mariotti et al., 1988; Högborg, 1997). Correlation between $\delta^{15}\text{N}-\text{NO}_3^-$ and sample temperature was significant ($r^2=0.76$; $p<0.01$), possibly indicating more N loss by volatilization or denitrification at higher temperatures (temperature data available for 9 of the 10 sites; data not shown). Packed-bed filter effluent $\delta^{18}\text{O}-\text{NO}_3^-$ ranged from -7.5 to -3.2‰, and were not correlated with $\delta^{15}\text{N}-\text{NO}_3^-$ values ($r^2=0.03$; not statistically significant).

3.4. Mass balance and isotope effects in maturing packed-bed filter systems

The ratio of Cl^- in packed-bed filter effluent to Cl^- in septic tank effluent, for the 86 matched (by date) pairs of ODEQ samples from the five systems in the maturing packed-bed filter network was 1.03 (median) and 1.06 (mean), consistent with a small overall net evapotranspiration effect (Table S2 in Supplementary data). Eight matched pairs of septic tank effluent and packed-bed filter effluent yielded an average $\delta^{18}\text{O}$ enrichment in packed-bed filter effluent of 0.24‰ relative to septic tank effluent (Table S3 in Supplementary data), which could be consistent with a minor amount of evaporation (isotopically fractionating) and transpiration (non-fractionating).

The greater apparent evapotranspiration in the mature packed-bed filter samples, compared with the maturing packed-bed filter samples, may reflect the relatively dry climate conditions during the mature packed-bed filter network sampling. Mature packed-bed filter samples were collected during October, 2001, a particularly dry October with precipitation in Bend of 0.74 cm for the month, compared with the calendar year total of 24.5 cm (National Climatic Data Center, 2005). Generally more arid conditions of Bend (location of mature packed-bed filter survey) compared with La Pine (location of maturing packed-bed filter monitoring) also may have contributed to these differences by affecting antecedent moisture in packed-bed filters.

N attenuation in the maturing packed-bed filters was most pronounced during the first several months of operation, as demonstrated by N/Cl^- ratios (Fig. 3; N/Cl^- ratios shown instead of N^* because many early-time septic tank effluent samples were not analyzed for Cl^-). Three packed-bed filters (53110A, 17346B, 50663F) yielded N/Cl^- ratios of <0.3 when sampled 2 to 7 months after installation, whereas N/Cl^- ratios typically were >1 in mature systems. Low N/Cl^- ratios were not due to an absence of septic tank effluent in the packed-bed filters because the packed-bed filter effluent samples contained sufficient Cl^- (several tens of milligrams per liter; Table S2 in Supplementary data) to indicate that septic tank effluent had passed through the packed-bed filters. These early-time data indicate that considerable N attenuation occurred in these packed-bed filters during the first months of operation. In the remaining two packed-bed filters, observed early-time N attenuation was comparable to that at later time. The substantial N attenuation in early-time data from some packed-bed filters is consistent with the results of column studies, and indicates that N loss to NH_4^+ sorption might occur in packed-bed filters early in their life cycle, but that sorption may be limited by saturation of sorption sites and/or development of nitrifying conditions. Some early-time N loss also might be accounted for by microbial assimilation during

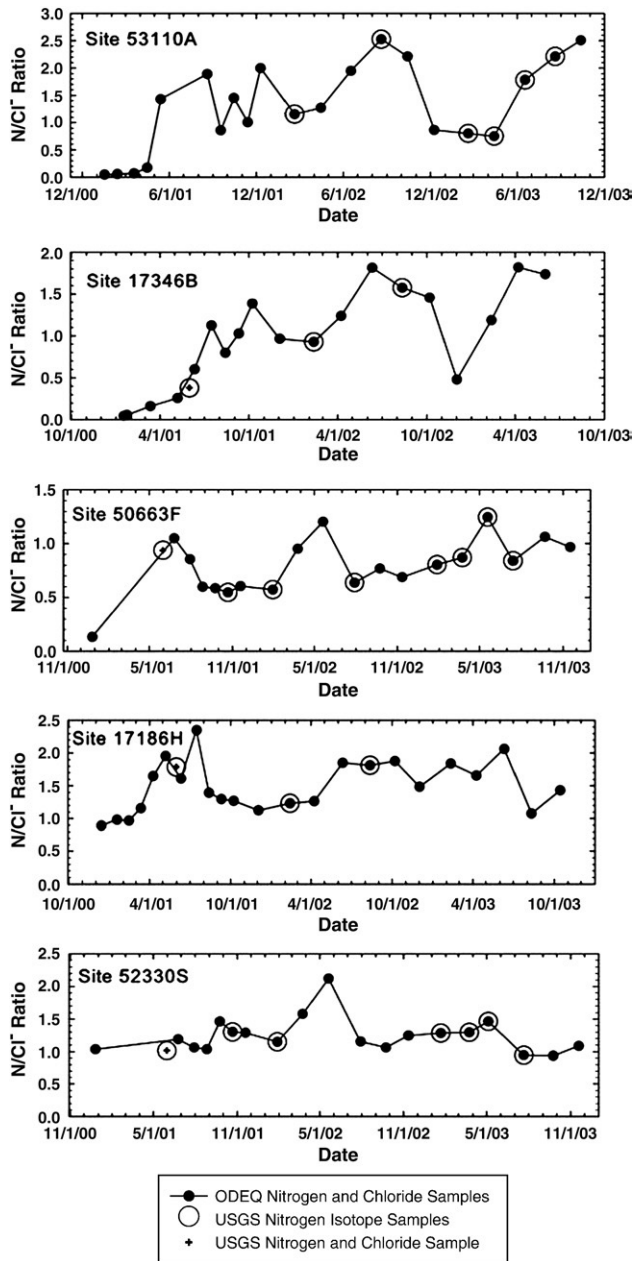


Fig. 3 – Maturing packed-bed filter N/Cl^- ratios over time. The horizontal axis begins at the point in time when the packed-bed filter began accepting septic tank effluent.

establishment of microbial communities in the packed-bed filters.

N attenuation also is indicated by samples collected after the first several months of monitoring, but N/Cl^- ratios appear to have reached a quasi-steady-state before the end of the first year of operation. Cl^- -normalized N losses in post-first-year samples averaged about 10% (Table 2). The difference in N attenuation between the post-first-year maturing packed-bed filter network samples (about 10%) and the mature packed-bed filter network samples (about 30%) could reflect system variability (e.g. water or nutrient loading, packed-bed filter sediment grain-size distribution) or seasonal variability (e.g. temperature or precipitation prior to sampling). The mature

network with greater average attenuation was near Bend, Oregon, which has the drier average climate.

A subset of samples from the network of five maturing systems was analyzed for isotopes (27 pairs of samples; Fig. 4, and Table S3 in Supplementary data). Isotope data from the first year of packed-bed filter operation are sparse. The first isotope sample from site 17346B (Fig. 3), with a N/Cl^- ratio of 0.38, had a relatively low $\delta^{15}N-NO_3^-$ value of +1.4‰, which could be consistent with a combination of isotopic fractionation during nitrification and sorption of isotopically enriched NH_4^+ . Other isotope data representing the first year of packed-bed filter operation plot beyond the apparent sorption phase in Fig. 3, and have $\delta^{15}N-NO_3^-$ values similar to those of post-first-year data.

In samples collected more than 1 year after commencement of packed-bed filter operation (21 pairs), $\delta^{15}N-NH_4^+$ values in septic tank effluent exhibited little variation, ranging from +4.2 to +5.1‰, with median and mean of +4.8‰ (Fig. 4a). Values of $\delta^{15}N-NO_3^-$ were more variable, ranging from +0.8 to +10.3‰, with median and mean of +6.5‰ (Fig. 4a). The average increase of 1.7‰ between NH_4^+ and NO_3^- in the maturing systems after 1 year of operation and the average 10% N attenuation (Table 2) are consistent with isotopic fractionation resulting from gaseous N (NH_3 , N_2 , and/or N_2O) losses.

$\delta^{18}O-NO_3^-$ values also were variable (Fig. 4b). Evaluating the set of post-first-year samples from the maturing packed-bed filter network as a whole, $\delta^{18}O-NO_3^-$ values did not increase systematically with increasing $\delta^{15}N-NO_3^-$, as is commonly observed in denitrifying ground water (Böttcher et al., 1990; Aravena and Robertson, 1998). Correlation between post-first-year $\delta^{18}O-NO_3^-$ and $\delta^{15}N-NO_3^-$ values was low ($r^2=0.04$) and not statistically significant. These data might indicate that NH_3 volatilization was more important than denitrification as a mechanism of N loss in these packed-bed filters, as fractionations from NH_3 volatilization will affect $\delta^{15}N$ but would not have a direct effect on $\delta^{18}O$ values established subsequently during nitrification. Upon closer inspection, though, relations between $\delta^{18}O-NO_3^-$ and $\delta^{15}N-NO_3^-$ values suggest the possibility that different processes might have occurred in bottomless and lined packed-bed filters. Post-first-year samples from lined packed-bed filters exhibited a positive correlation

Table 2 – Values of N^* (ratio of Cl^- -normalized N in packed-bed filter effluent to Cl^- -normalized N in septic tank effluent, Eq. (1)) in maturing packed-bed filter network

Packed-bed filter	N^*		n
	Mean	Median	
53110A	1.00	0.99	13
17346B	0.90	0.90	11
50663F	0.76	0.73	13
17186H	0.89	0.83	13
52330S	0.93	0.90	12

Analysis restricted to samples collected more than one year after commencement of packed-bed filter operation, to avoid early-time data that might be associated with sorption; complete data in Table S2 in Supplementary data.

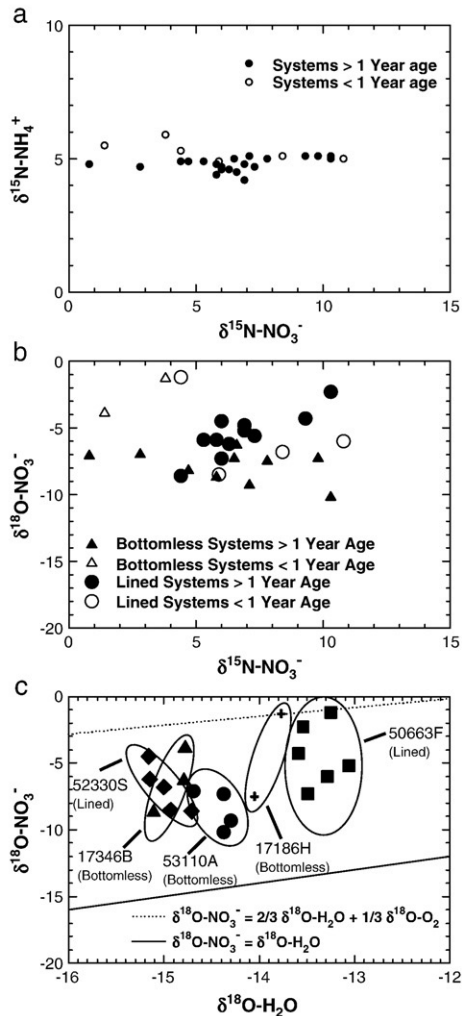


Fig. 4 – Relations among isotopic data in the maturing packed-bed filter network (data from Table S3 in Supplementary data). (a) $\delta^{15}\text{N-NO}_3^-$ in packed-bed filter effluent and $\delta^{15}\text{N-NH}_4^+$ in septic tank effluent collected simultaneously. (b) $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ in packed-bed filter effluent. (c) $\delta^{18}\text{O-H}_2\text{O}$ and $\delta^{18}\text{O-NO}_3^-$ in packed-bed filter effluent.

($r^2=0.71$; $p<0.01$), whereas post-first-year samples from bottomless packed-bed filters exhibited weak, negative correlation ($r^2=0.19$; not statistically significant) (Fig. 4b). These relations could reflect the preferential existence of denitrification in the lined packed-bed filters. However, gravel (>15 cm) placed on top of the liner in lined packed-bed filters would reduce the potential for development of a capillary fringe above the liner in the bottom of the sand material that otherwise might facilitate denitrification. Furthermore, the relation between $\delta^{18}\text{O-NO}_3^-$ and $\delta^{15}\text{N-NO}_3^-$ values for lined packed-bed filters is more complex when young (first-year) samples are considered (Fig. 4b); it is not clear if this reflects a time lag for development of denitrifying microbial populations, or if the larger number of samples simply provides a more comprehensive picture of the true complexity in these systems.

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of H_2O range from about -116 to -102‰ and -15.3 to -13.1‰ , respectively. These values differ consistently from site to site (Fig. 4c), and they do not appear to record seasonal isotopic variations in precipitation (Table S3 in Supplementary data). More than 90% of the water passing through these packed-bed filters is domestic well water, which is derived from local ground water (Section 3.2). The $\delta^{18}\text{O-NO}_3^-$ values also do not appear to be related to seasonality (Table S3 in Supplementary data). Some of the variation in $\delta^{18}\text{O-NO}_3^-$ could be due to variation in the $\delta^{18}\text{O}$ of H_2O during nitrification, but the variation in $\delta^{18}\text{O-NO}_3^-$ is greater (factor of four) than the variation in $\delta^{18}\text{O}$ of H_2O . As a group, the $\delta^{18}\text{O-NO}_3^-$ values plot between a hypothetical line representing 100% unfractionated $\text{H}_2\text{O-O}$ as a source of O incorporated in NO_3^- during nitrification (Sigman et al., 2005) and a hypothetical line representing a mixture of 2/3 $\text{H}_2\text{O-O}$ and 1/3 atmospheric $\text{O}_2\text{-O}$ as sources of O incorporated in NO_3^- during nitrification (Amberger and Schmidt, 1987) (Fig. 4c). Values of $\delta^{18}\text{O-NO}_3^-$ from the mature packed-bed filter network fall between these hypothetical lines, too (Table 1). Both the variability of $\delta^{18}\text{O-NO}_3^-$ values and the deviation of these values from the 2/3 $\text{H}_2\text{O-O}$ 1/3 $\text{O}_2\text{-O}$ model could be due to fractionation of O isotopes derived from either H_2O or O_2 , as has been observed with O isotopes during FeS_2 oxidation to SO_4^{2-} (Balci et al., 2007), or to partial isotopic equilibration between $\text{H}_2\text{O-O}$ and intermediate nitrogen oxide species during N oxidation (Casciotti et al., 2007).

3.5. From septic tank to ground water

Following discharge from septic tanks, N may be affected by dilution with precipitation, concentration by evapotranspiration, NH_4^+ sorption, NH_3 volatilization, nitrification, and(or) denitrification. Results of this study indicate that after several months of packed-bed filter operation, NH_4^+ sorption appeared to be minimal. Nitrification in packed-bed filters was efficient, with about 98% of N exiting packed-bed filter sediments occurring as NO_3^- . Apparent net gaseous N (NH_3 , N_2 , and(or) N_2O) loss in packed-bed filters averaged 10–30% after accounting for dilution with precipitation and concentration by evapotranspiration.

Combining results from all of the systems studied, septic tank effluent $\delta^{15}\text{N-NH}_4^+$ values were relatively uniform and averaged $+4.9\text{‰} \pm 0.4\text{‰}$ (1 σ). Values of $\delta^{15}\text{N-NO}_3^-$ from packed-bed filter effluent from the mature network and the post-first-year maturing-network samples were more variable ($+0.8$ to $+14.4\text{‰}$) and averaged $+7.2\text{‰} \pm 2.6\text{‰}$; $\delta^{18}\text{O-NO}_3^-$ values ranged from -10.2 to -2.3‰ and averaged $-6.4\text{‰} \pm 1.8\text{‰}$. The large database of $\delta^{15}\text{N-NO}_3^-$ values summarized here is consistent with regional data from the underlying aquifer near La Pine, supporting the hypothesis that NO_3^- there is primarily from septic tank effluent (Hinkle et al., 2007). Ground water samples from the oxic zone of this aquifer, unaffected by denitrification in the saturated zone, had $\delta^{15}\text{N-NO}_3^- = +6.6\text{‰} \pm 2.1\text{‰}$ ($n=9$) and $\delta^{18}\text{O-NO}_3^- = -5.1\text{‰} \pm 2.8\text{‰}$ ($n=5$) (Hinkle et al., 2007; new data from this study).

We interpret the variability of $\delta^{15}\text{N-NO}_3^-$ values to reflect variability in the relative rates, efficiencies, and isotope fractionation effects of transport, mineralization, NH_3 volatilization, nitrification, and denitrification within the packed-bed filters at different times and places, whereas the average $\delta^{15}\text{N}$ isotopic difference between the incoming NH_4^+ and

outgoing NO_3^- are interpreted to reflect net, average N loss by NH_3 volatilization and/or N_2 or N_2O degassing during nitrification/denitrification. Variability in $\delta^{18}\text{O}-\text{NO}_3^-$ values that is largely independent of seasonality and of variability in $\delta^{18}\text{O}-\text{H}_2\text{O}$ values, and $\delta^{18}\text{O}-\text{NO}_3^-$ composition intermediate between 2/3 $\text{H}_2\text{O}-\text{O}$ and 100% $\text{H}_2\text{O}-\text{O}$, may reflect differences in the nitrification process, partial isotopic equilibration among O-containing species during development of $\delta^{18}\text{O}$ signatures in wastewater NO_3^- , or subsequent fractionations. Some of this variability could possibly be related to changes in the saturation state of sediments in the packed-bed filters or to transient abundances of intermediate nitrogen oxides during nitrification. Temporal variability in packed-bed filter $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ values demonstrates a potential limitation of relying on isolated samples of septic tank-derived NO_3^- in studies of septic tank-impacted environments.

Although this study was focused on mounded packed-bed filter treatment systems, it is possible that similar processes occur where septic tank effluent passes through naturally emplaced unsaturated-zone sediment. A literature review by Fogg et al. (1998) indicated that unsaturated-zone water impacted by septic tank effluent typically had $\delta^{15}\text{N}-\text{NO}_3^-$ values of +7 to +15‰. Additional studies may indicate if there are systematic reasons for the large range of reported $\delta^{15}\text{N}$ values for septic tank-derived NO_3^- in unsaturated-zone and ground water. To date, characterization of $\delta^{18}\text{O}$ of septic tank-derived NO_3^- has been scarce, and additional $\delta^{18}\text{O}$ characterization of this important NO_3^- source term may indicate if the relatively low values reported here are typical or unusual. This is important because previously reported data produced by different isotopic analytical methods in the absence of reference materials may not be comparable (Révész and Böhlke, 2002; Böhlke et al., 2003). Further work within the unsaturated zone might also help clarify specific N loss mechanisms and isotopic characteristics of NO_3^- delivered to the water table.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.scitotenv.2008.08.036.

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